



TITLE:

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AUTHOR(S):

Negoro, Y; Kimoto, T; Matsunami, H

CITATION:

Negoro, Y ...[et al]. Stability of deep centers in 4H-SiC epitaxial layers during thermal annealing. Applied Physics Letters 2004, 85(10): 1716-1718

ISSUE DATE:

2004-09-06

URL:

<http://hdl.handle.net/2433/24195>

RIGHT:

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Stability of deep centers in 4H-SiC epitaxial layers during thermal annealing

Y. Negoro,^{a)} T. Kimoto, and H. Matsunami

Department of Electronic Science and Engineering, Kyoto University, Kyotodaigaku-katsura, Nishikyo-ku, Kyoto 615-8510, Japan

(Received 25 February 2004; accepted 7 July 2004)

N-type epitaxial 4H-SiC layers grown by hot-wall chemical vapor deposition were investigated with regard to deep centers by capacitance-voltage measurements and deep level transient spectroscopy (DLTS). The DLTS spectra revealed that the concentrations of deep centers were reduced by one order of magnitude by annealing at 1700 °C, compared to those in an as-grown material. The $Z_{1/2}$ center with an energy level of 0.59 ± 0.03 eV and the $EH_{6/7}$ center with an energy level of 1.66 ± 0.11 eV below the conduction band edge are annealed out at a temperature of 1700 °C or higher. © 2004 American Institute of Physics. [DOI: 10.1063/1.1790032]

Silicon carbide (SiC) is an attractive material for high-power, high-temperature, and high-frequency devices, owing to its superior properties such as wide band gap, high breakdown field, high thermal conductivity, and high saturation electron drift velocity.¹ 4H-SiC has been regarded as the most promising polytype for vertical-type high-voltage applications, owing to its higher bulk mobility and smaller anisotropy. Several power devices made of 4H-SiC have recently outperformed conventional Si devices,² due to remarkable progress in SiC growth technology as well as device processing techniques. Despite the improvements in epitaxial quality in past years, the knowledge and understanding of electrical properties of deep centers are still limited. Deep centers in the band gap may adversely affect device performances, because the carrier lifetime is often limited by deep centers in the band gap acting as recombination centers. Therefore, reduction of deep centers is of great importance as well as is the understanding of the centers.

In this letter, the authors present thermal stability of deep centers in as-grown *n*-type 4H-SiC (0001) epitaxial layers grown by chemical vapor deposition (CVD) using a chimney-type hot-wall CVD reactor. The electrical properties of deep centers are characterized using deep level transient spectroscopy (DLTS).

The epitaxial growth was performed on a commercial *n*-type 8° off-axis 4H-SiC (0001) wafer in a $\text{SiH}_4\text{-C}_3\text{H}_8\text{-H}_2$ system at 1700 °C for 3 h.³ The substrates were placed in a SiC-coated graphite susceptor heated by radio-frequency induction. The C/Si ratio was 0.62 with a SiH_4 flow rate of 16.3 sccm at a reactor pressure of 100 Torr. The growth rate of epitaxial layers reported here was about 10 $\mu\text{m/h}$ with a H_2 flow rate of 5 slm. In the present growth system, the growth under a low C/Si ratio below 0.7 results in the high concentration of deep centers.³ These particular samples were extensively investigated, because a relatively high concentration of deep traps in the epitaxial layers enables easy detection of traps in the wide range of trap concentration after thermal annealing. Note that a low trap concentration below $1 \times 10^{13} \text{ cm}^{-3}$ can be obtained by increasing the C/Si ratio during epitaxial growth.

The net donor concentration was determined by capacitance-voltage measurements on a Ni/4H-SiC Schottky structure with a probe frequency of 1 MHz. Backside ohmic contacts for *n*-type substrates were formed with Ag paste. DLTS spectra were acquired on Ni/4H-SiC Schottky diodes with a 0.8 mm diameter. The reverse bias was kept at -5 V, and the pulse height applied during the DLTS measurements was 5 V. The transient length used in this study was 0.2 s. For the analysis of DLTS spectra, a Fourier transform analysis⁴ of the measured transients was employed, together with an Arrhenius plot analysis for the determination of capture cross section, energy level, and trap concentration. Temperature-independent capture cross section was assumed when analyzing the DLTS data.

After the DLTS measurements on as-grown materials, Ni Schottky contacts as well as backside Ag paste on 4H-SiC were removed. And then, annealing was performed in an Ar ambient using a CVD reactor. The annealing temperatures (periods) were 1600 °C (30 min), 1700 °C (30 min), 1750 °C (30 min), and 1800 °C (15 min). Each sample was annealed at one temperature. Note that before the annealing, all samples investigated here showed almost the same concentrations of net donor and deep centers because these samples were prepared in the same CVD run. After annealing at each temperature, Ni Schottky contacts were again deposited on the samples, and ohmic contacts were formed with Ag paste for subsequent capacitance-voltage and DLTS measurements.

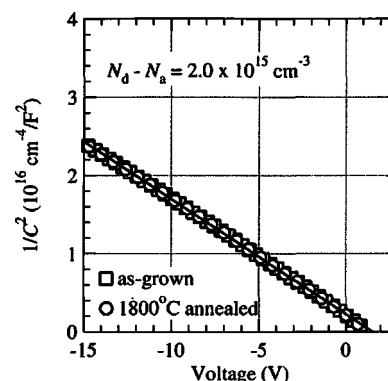


FIG. 1. The $1/C^2$ - V characteristics of (a) Ni/as-grown and (b) Ni/1800 °C-annealed 4H-SiC Schottky structures.

^{a)} Author to whom correspondence should be addressed; electronic mail: negoro@semicon.kuee.kyoto-u.ac.jp

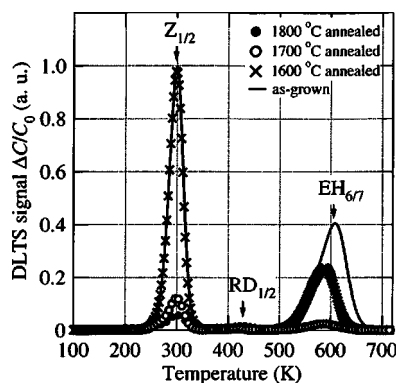


FIG. 2. DLTS spectra of as-grown and annealed 4H-SiC epitaxial layers.

Figure 1 shows the $1/C^2$ - V characteristics of (a) Ni/as-grown and (b) Ni/1800 °C-annealed 4H-SiC Schottky structures, where C is the depletion-region capacitance per unit area. The linearity in the $1/C^2$ - V plots in the wide voltage range indicates that the epitaxial layer has a uniform doping profile with a net donor concentration of $2 \times 10^{15} \text{ cm}^{-3}$. There was no difference in the net donor concentration between as-grown and annealed epitaxial layers.

DLTS spectra of as-grown and annealed epitaxial layers are shown in Fig. 2. One of the strong peaks at about 300 K can be correlated to the well-known $Z_{1/2}$ center⁵ with an energy level of $0.59 \pm 0.03 \text{ eV}$ below the conduction band edge with a temperature-independent capture cross section of $4\text{--}6 \times 10^{-16} \text{ cm}^2$. The as-grown epitaxial layer contains the $Z_{1/2}$ center with a concentration of $1.2 \times 10^{14} \text{ cm}^{-3}$. The $Z_{1/2}$ center concentration stayed unchanged after annealing at 1600 °C. For the 1700 °C-annealed epitaxial layer, however, the concentration of the $Z_{1/2}$ center became approximately one order of magnitude lower than that of the as-grown epitaxial layer.

Figure 3 shows the annealing-temperature dependence of net donor and trap concentrations. The concentration of the $Z_{1/2}$ center gradually decreases with the increase of annealing temperature above 1700 °C. The concentration could be reduced down to $7.3 \times 10^{12} \text{ cm}^{-3}$ by annealing at 1800 °C. There was no significant difference in both the trap energy and the capture cross section of the $Z_{1/2}$ center between as-grown and annealed epitaxial layers.

One of the open questions about the $Z_{1/2}$ center is whether the center is thermally stable or not. Some reports have shown that the $Z_{1/2}$ center is thermally stable even at

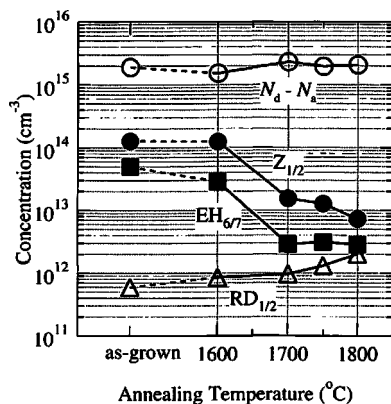


FIG. 3. Annealing temperature dependence of net donor concentration and trap concentrations for 4H-SiC epitaxial layers.

2015 °C.⁶ In contrast, it has also been reported that the center in the electron-irradiated 4H-SiC was annealed out at 1200 °C.⁷ The electron-irradiated 4H-SiC (electron dose: $1 \times 10^{15}\text{--}3 \times 10^{17} \text{ cm}^{-2}$) contains much more vacancies and interstitials than as-grown 4H-SiC. This may easily bring the annealing out of the $Z_{1/2}$ center at relatively low temperatures, assuming that the center is related to vacancies and interstitials. The experimental results presented here show that the $Z_{1/2}$ center is thermally unstable at a temperature of 1700 °C or higher, even in nonirradiated as-grown 4H-SiC. It is unknown for the moment whether the $Z_{1/2}$ center is a purely intrinsic defect or contains both intrinsic defects and extrinsic impurities. Many candidates for a part of origins have been proposed through experimental results from DLTS study on virgin epitaxial 4H-SiC, such as silicon vacancy,⁶ carbon vacancy,⁸ divacancy,⁹ silicon antisite,⁸ or nitrogen with interstitial carbon.¹⁰ Recently Storasta *et al.* have experimentally shown that the concentration of the $Z_{1/2}$ center in electron-irradiated 4H-SiC doped with phosphorus donors exceeds the nitrogen concentration by one order of magnitude.¹¹ From their report, it can be concluded that no nitrogen atoms participate in the formation of the $Z_{1/2}$ center. Possible origins of $Z_{1/2}$ center and other deep levels will be later discussed, based on annealing experiments described here.

There seem to be a few trap centers correlated to the peaks around 350–500 K. The peak at around 420 K may be ascribed to the $RD_{1/2}$ center with an activation energy of $0.95 \pm 0.05 \text{ eV}$ with a capture cross section of about $5\text{--}8 \times 10^{-14} \text{ cm}^2$. The concentrations of these trap centers, however, increase slightly with the increase of annealing temperature as shown in Fig. 3.

The peak at about 600 K shown in Fig. 2 can be correlated to the $EH_{6/7}$ center¹² with an energy level of $1.66 \pm 0.11 \text{ eV}$ below the conduction band edge. The center was observed in electron-irradiated 4H-SiC for the first time by Hemmingsson *et al.*¹² The $EH_{6/7}$ center has a concentration of $4.9 \times 10^{13} \text{ cm}^{-3}$ and a relatively large capture cross section of $1\text{--}4 \times 10^{-13} \text{ cm}^2$ for the as-grown epitaxial layer. This defect center is of great importance, because the location at midgap and the large capture cross section should greatly influence the generation and recombination of carriers. The concentration of this center was slightly reduced even by 1600 °C annealing. For 1800 °C annealing, the concentration decreased to $2.8 \times 10^{12} \text{ cm}^{-3}$ (Fig. 3), which is one order of magnitude lower than that for an as-grown material. The capture cross section of the center in the annealed epitaxial layers increased by a factor of 1–2 orders of magnitude, compared to that in the as-grown epitaxial layers. The peak of the center shown in Fig. 2 slightly shifts to a lower temperature by the annealings. This shift may be attributed to the following causes. The $EH_{6/7}$ center consists of two or more peaks, and one of the peaks at a higher temperature was annealed out. The increase of the capture cross section is speculated to be due to the reconfiguration of defect complexes.

As shown in Fig. 3, both of the concentrations for the $Z_{1/2}$ and the $EH_{6/7}$ centers decreased with increasing annealing temperature. The annealing behaviors of the centers agree with a recent report by Zhang *et al.*¹⁵ In their paper, the $Z_{1/2}$ concentration in 4H-SiC (0001) epitaxial samples annealed at 1650 °C decreased and the concentration after the annealing remained in the high 10^{12} to low 10^{13} cm^{-3} range, AIP license or copyright, see <http://apl.aip.org/apl/copyright.jsp>

compared with the initial concentration of low 10^{13} to low 10^{14} cm^{-3} . In terms of the $EH_{6/7}$ center, they have reported that the original DLTS peak of the center in the as-grown sample disappeared after annealing, while another smaller peak appeared at a slightly lower temperature in the DLTS spectra. It should also be noted that the formation of both the $Z_{1/2}$ and $EH_{6/7}$ centers is suppressed by CVD growth under a C-rich condition.^{13,14} Recently, Storasta *et al.* reported a DLTS study on 4H-SiC (0001) epilayers irradiated with low-energy (80–300 keV) electrons, by which only C atoms are displaced.¹⁶ They speculated that the origin of the $EH_{6/7}$ center might be a C vacancy, because the $EH_{6/7}$ center is one of the most dominant traps observed for such samples, and the activation energy for this center agrees well with the energy position measured for a positively charged carbon vacancy in *p*-type 4H-SiC detected by photoelectron spin resonance.¹⁷ If the $EH_{6/7}$ center is, or contains, a C vacancy, the growth-condition dependence of $EH_{6/7}$ center formation^{13,14} is easily explained because less C vacancies should be generated under a C-rich growth condition. From the annealing experiment and the growth-condition dependence, it might be reasonable that both the $Z_{1/2}$ and $EH_{6/7}$ centers are different defect complexes but contain the same origin in the structure like a C vacancy. In order to reveal the microscopic structures, further investigation is required.

In summary, DLTS investigations of as-grown and annealed 4H-SiC epitaxial layers have been carried out. By annealing at 1700 °C or higher temperature, the concentration of the $Z_{1/2}$ and $EH_{6/7}$ centers became one order of magnitude lower than that in the as-grown epitaxial layers, although the net donor concentration of epitaxial layer is kept constant. These results indicate that the $Z_{1/2}$ and $EH_{6/7}$ centers can be annealed out by annealing at 1700 °C or higher temperature. On the other hand, the concentration of the $RD_{1/2}$ center increases slightly by 1700 °C annealing.

The authors thank K. Fujihira, now at Mitsubishi Electric Co., for epitaxial growth. The authors also thank Kyoto University Venture Business Laboratory for the use of measurement equipment. This work was partially supported by a Grant in Aid for the 21st Century COE program 14213201, the Ministry of Education, Culture, Sports, Science and Technology of Japan, and also by TEPCO Research Foundation.

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